

Elevated Temperature Aging of HIPS

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Synopsis

The effects of aging at 85°C on a rubber-modified polystyrene (HIPS) have been studied as a function of aging time in both air and nitrogen. Four different types of physical measurements were carried out on the aged samples. These included mechanical relaxation measurements, tensile stress-strain measurements, creep measurements at several stresses, and measurements of fatigue lifetime under applied tension-compression stress. Aging in nitrogen is largely a physical aging process and results in higher modulus, higher tensile strength, and longer delay times to the onset of accelerating creep deformation. But tensile ductility and fatigue lifetime tend to reduce, and there is no change in location of T_g of the rubber phase. Aging in air involves both chemical and physical aging, and the changes that occur depend on which process dominates. For long-time aging of 150 h or more, the rubber-phase T_g is shifted to higher temperatures and the associated loss peak is broadened due to crosslinking. Also, the tensile strength, tensile ductility, creep delay time, and fatigue life all reduce. These effects are attributed to oxidative attack and embrittlement. SEM micrographs reveal variations in fracture surface morphology due to the mode of testing and to the aging medium.

Introduction

Glassy polymers are in a nonequilibrium state as a result of being cooled through the glass transition temperature (T_g) at a finite rate. They possess excess enthalpy and excess volume compared to samples cooled infinitely slowly. Subsequent annealing at temperatures below T_g , a process referred to as physical aging, brings the polymer closer to its equilibrium state and results in changes in relaxation magnitude as well as a shift of the retardation spectrum to longer times.^{1,2} Significant changes also take place in mechanical properties. These generally include an increase in density, modulus, and tensile strength and a decrease in ductility and impact strength. Thermal history is thus an important variable in many glassy polymers. This is demonstrated, for example, by the studies of Matsuoka and Bair³ who measured the stress relaxation behavior of polystyrene (PS) specimens previously subject to annealing at 90°C (10°C below T_g) for times varying from 1 to 150 h. For each decade increase in annealing time, the relaxation curve was shifted to longer times by approximately one decade.

On the other hand, it is also well established that continued exposure to elevated temperatures, or even long-time exposure to sunlight and weathering at ambient temperature, may produce, depending upon the specific prevailing conditions and the composition of the polymer, severe degradation of mechanical properties. This process is referred to as chemical aging, as it usually involves chemical interaction between oxygen and the component atoms of the polymer

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chain. The effect is particularly severe if double bonds are present, as in most elastomers, or when unsaturated rubbers, such as polybutadiene, are used as reinforcing components and toughening agents in glassy polymers.⁴ Chemical aging, resulting from thermal or photo-oxidation, also results in the development of oxidation products such as carbonyl groups, water, and ketones, in yellowing of the samples, in decrease of double bond content, and in embrittlement as a result of reduction in molecular weight or of crosslinking. Chemical aging effects have been observed and studied in various rubber-modified polymers, such as high-impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS), by various authors.⁴⁻⁷

In the present study, the changes in mechanical relaxation behavior and the changes in certain mechanical properties, such as tensile strength, creep resistance, and fatigue performance, of a rubber-modified polystyrene are investigated as a function of annealing time at 85°C. Also, to aid in our understanding of the relative influence of physical aging effects vs. chemical aging effects, tests have been made both on samples aged in air and samples aged in nitrogen. For these latter samples, oxidative degradation effects should be greatly reduced, if not entirely eliminated; hence, the observed changes should be largely those resulting from physical aging alone. The influence of annealing in air, but not in nitrogen, on fatigue lifetime of HIPS has received some attention.⁸ An aging temperature of 85°C was selected for the present studies for two reasons. First, aging effects are accelerated by annealing at elevated temperatures. Secondly, by annealing at a temperature some 10–15°C below T_g , comparison of our results with those of other investigators^{3,8} is facilitated.

EXPERIMENTAL

The rubber-modified HIPS material was received in the form of 1/2-in.-diam. extruded rods. From the results of tensile tests made on samples machined from these rods and from observation of fracture surfaces by scanning electron microscopy, the rubber-phase volume of this material is estimated to be about 30%. Also, the rubber particle size, which varies from about 0.5 to 5 μm , has an average value in the range 2.5–3 μm .⁸

The test samples were annealed at 85°C in an air oven or, in some cases, in the presence of nitrogen, for varying times ranging from 1 to 150 h. For the tensile, creep, and fatigue studies, test samples were machined from the as-received extruded rods. They were threaded at the ends to engage the grips, and the gauge length and diameter were 1.27 cm and 5.08 mm, respectively. For the mechanical relaxation tests, rectangular samples were cut from compression-molded sheets of HIPS pellets. These samples were about 1.5 cm in length, 0.8 cm in width, and about 100 μm in thickness.

The mechanical relaxation tests were made in alternating tension at low strain amplitude on a Piezotron apparatus at a frequency of 3 Hz. The temperature range studied varied from –150 to 0°C, and the heating rate was 2°C/min. From these measurements, values of the storage modulus E' , the loss modulus E'' , and the tangent of the loss angle $\tan \delta$ were obtained as a function of temperature.

The tensile tests were performed on an Instron apparatus at a deformation rate of 12.7×10^{-2} cm/min. Two or three separate samples were tested for each aging time; and from the load deflection curves, the average yield strength and

the average elongation to fracture were determined. The drop in stress, after the yield stress is reached, a measure of the extent of strain softening of the sample, was also noted.

The creep tests were performed on an Instron servohydraulic apparatus. Most of the tests were carried out at a constant stress of 13.8 MPa (2000 psi); some were also carried out at 17.2 MPa (2500 psi). The initial load was applied over a 1-s period and was then maintained constant while the elongation was monitored as a function of time. From the plot of creep elongation vs. time, a creep delay time t_d could be determined. In times below t_d , the elongation increased only slowly with time; while at times above t_d , there was a significant increase in rate of creep deformation. For each time of annealing at 85°C, two or more samples were tested and the average delay time then determined from these measurements. For samples that fractured during the creep test, rupture time t_r and elongation or strain to rupture ϵ_r were also recorded.

Fatigue tests were made in alternating tension-compression at a stress amplitude of 13.8 MPa and at a frequency of 21 Hz. These tests were carried out on an Instron servohydraulic apparatus. At this test frequency, there is some specimen heating due to hysteresis effects. By use of a Barnes infrared detector focused on the sample, the temperature rise in the specimen at fracture for an alternating stress amplitude of 13.8 MPa was estimated to be 4–5°C.⁹ Prior to testing, all of the fatigue specimens were carefully polished in a manner similar to that used for polystyrene specimens in order to reduce the scatter in results due to variations in surface finish.^{10,11} For each time of annealing, four to five specimens were usually tested and the mean fatigue life determined by averaging the various $\log N_f$ values, where N_f is the number of cycles to failure for each specimen.

For many of the samples that were fractured in tension, in creep and in fatigue, the fracture surface was examined by light microscopy and by use of an Etec scanning microscope (SEM). Prior to SEM examination, the fracture surfaces were coated with a thin layer of gold-palladium.

RESULTS AND DISCUSSION

Mechanical Relaxation Tests

When the mechanical relaxation behavior of two-phase rubber-modified polymers is investigated over a wide temperature range, the $\tan \delta$ -vs.- T curves generally exhibit two principal loss peaks: one at low temperatures associated with the glassy to rubbery transition of the rubber phase, and one near 100°C associated with the T_g of the PS matrix phase.⁴ The location of the main rub-

TABLE I
Rubber Phase T_g Values

Aging medium	T_g , °C				
	0 h ^a	4 h	24 h	72 h	150 h
Air	-95.6	-95.0	-93.8	-93.2	-81.4
N ₂	-95.6	—	—	—	-94.8

^a Hours of annealing at 85°C.

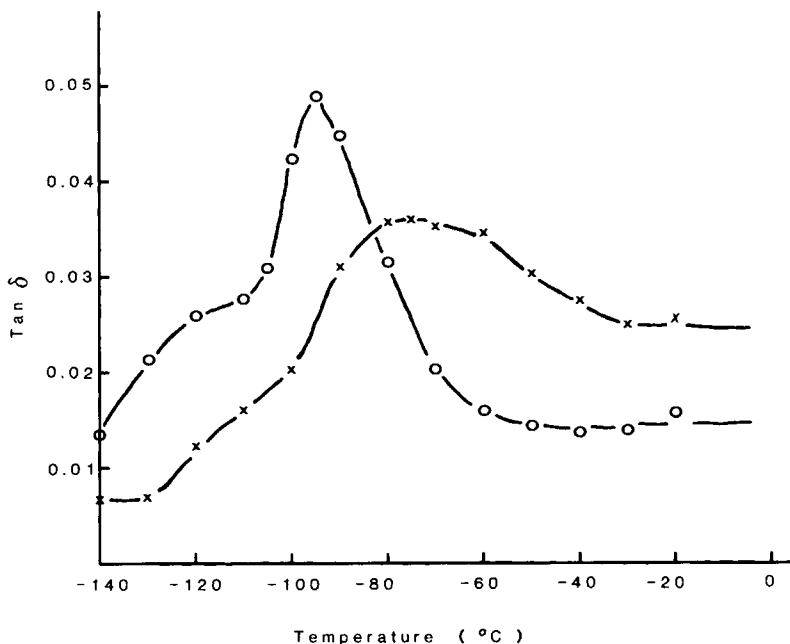


Fig. 1. $\tan \delta$ vs. temperature for an untreated HIPS sample (O) and for a sample aged 150 h in air at 85°C (x).

ber-phase T_g transition, from our measurements made at 3 Hz on unannealed samples, was found to be about -95°C . This is in good agreement with the value reported by Baccaredda and Butta¹² and about 7°C higher than the value reported by Trick¹³ for polybutadiene rubber.

With increasing time of air annealing at 85°C , the low-temperature loss peak is found to shift upward in temperature. This is indicated by the data on Table I, where the listed T_g values have been determined from the maximum in the loss modulus data.

Upon aging in air, there is a small upward shift with annealing times to about 72 h. Then, with increasing aging time, a more dramatic rise occurs. After 150 h of aging, the loss peak has shifted to higher temperatures by about 14°C . If the samples are aged in N_2 instead of air, there is less than a 1°C upward shift, even for 150 h. of aging, and this is within the experimental error of our measurements. The upward shift upon annealing in air is attributed to oxidatively induced crosslinking through interaction of atmospheric oxygen with the double bonds present in polybutadiene.

The result of this crosslinking is to shift the loss peak to higher temperatures and to broaden it. This is evident from Figure 1, where internal friction ($\tan \delta$) data are shown for both the unaged sample and for the sample aged 150 h in air. A somewhat similar upward shift, accompanied by peak broadening, has also been observed on HIPS samples exposed to ultraviolet light from a sun-lamp¹⁴ and in crosslinked HIPS containing a small amount of sulfur.¹⁵

For the sample aged 150 h in N_2 , the modulus and $\tan \delta$ data are shown in Figure 2. The general shape of the damping peak and the temperature location of the maximum value are essentially the same for the unannealed sample. The

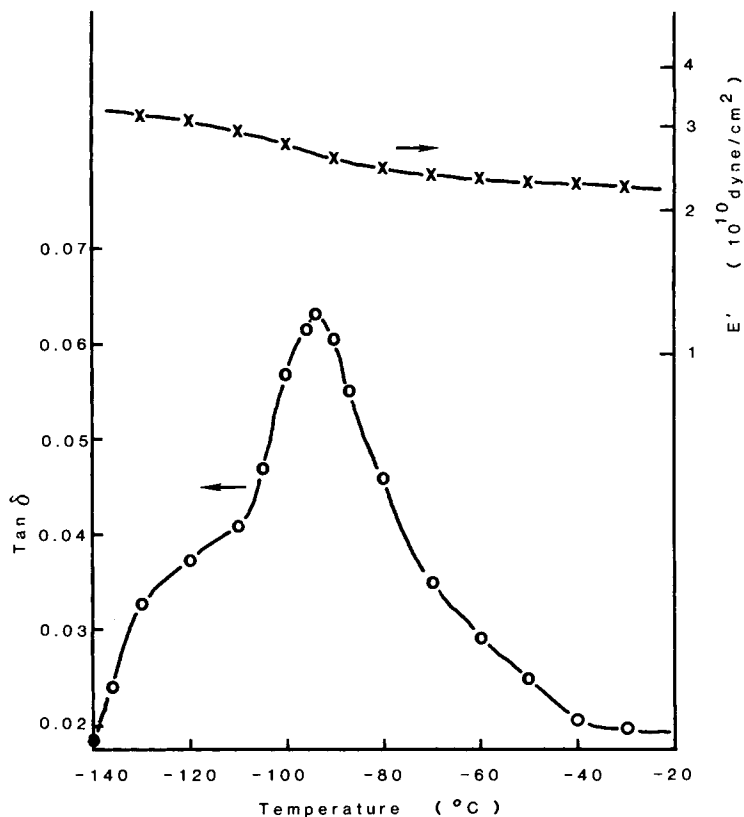


Fig. 2. E' and $\tan \delta$ vs. temperature for a HIPS sample aged 150 h in N_2 at $85^\circ C$.

modulus values over the temperature range from -140 to $-40^\circ C$ are higher by about 5–8% for the sample aged in nitrogen. This increase in modulus is a typical indication of a physical aging effect. In both Figures 1 and 2, there appears to be a low-temperature shoulder near $-120^\circ C$. The cause of this is not known. It may indicate some inhomogeneity within the rubber phase itself, with perhaps the shoulder arising from the presence of some low-molecular-weight lubricant. A small broad peak in $\tan \delta$ in the vicinity of $-120^\circ C$ is also evident in the data of Cigna for a HIPS sample; but when the styrene phase was separated from the rubber phase and tested, this peak was not present.¹⁶

TABLE II
Effect of Aging at $85^\circ C$ on Tensile Properties of HIPS

Aging medium	Time of aging, h	Yield strength, MPa	Elongation, mm	Yield drop, %
None	—	19.8	10.2	14.5
Air	1	19.9	8.66	16.4
	15	20.2	8.64	18.1
	150	19.3	6.25	20.1
N_2	150	20.2	6.53	16.4

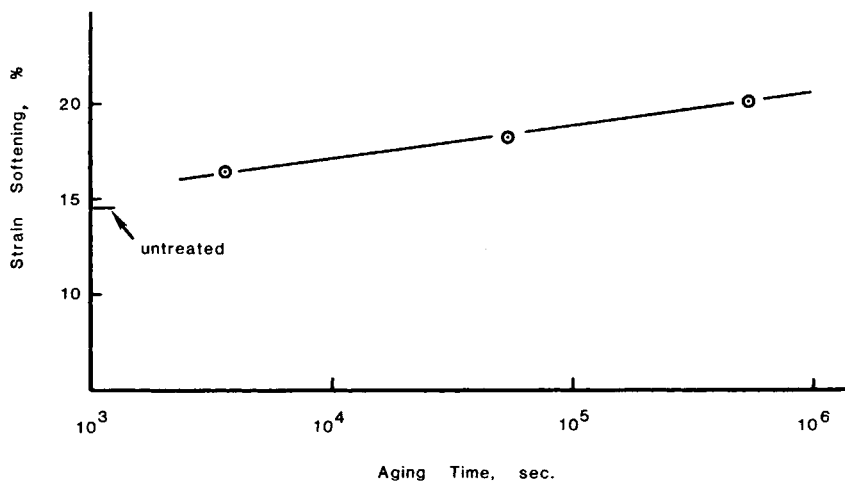


Fig. 3. Strain softening vs. aging time at 85°C for HIPS samples tested in tension.

Tensile Measurements

The results of the tensile measurements made on both unaged samples and on samples aged at 85°C are shown in Table II. Upon aging in air, there is a slight increase in yield strength up to about 15 h of aging, and this is accompanied by a drop in ductility. These effects are attributed to a slight material densification as the molecular chain structure rearranges itself upon physical aging. This leads to an increase in relaxation times and to a release of some of the excess enthalpy and volume. However, after annealing for longer times, as 150 h in air, the yield strength reduces and falls below the value for the unannealed control samples. The ductility is also considerably reduced, and after 150 h of air aging, it has fallen by almost 40%. These changes are indicative of some chemical aging, such as oxidative embrittlement. Chemical attack by oxygen, which affects primarily the surface, is known to lower the energy for crack initiation.⁵ Hence, both ductility and toughness of the polymer (area under the stress-strain curve) are considerably reduced.

Upon aging for 150 h in nitrogen, the tensile strength and elongation to fracture are about 5% higher than values obtained on aging in air. The tensile strength is also above that of the control samples, but the ductility is considerably reduced. Aging in N₂ should significantly reduce thermal oxidative effects; hence, the results obtained are essentially indicative of physical aging only. An increase in yield strength, upon aging for 10 days under vacuum at 100°C, has also been observed in polycarbonate.¹⁷

The data presented in the last column of Table II show that the degree of strain softening (defined, in percent, as the drop in stress after onset of yielding, $\Delta\sigma_y$, divided by σ_y) also depends on the aging treatment given to the rubber-modified polystyrene. Upon aging in air, as Figure 3 shows, the degree of strain softening increases linearly with log of aging time. Clearly, the aging treatment is affecting the plastic instability of the material. Somewhat similar effects have been noted by Adam et al.¹⁸ upon annealing PC at 120–130°C and by Cross et al.¹⁹ upon tensile testing annealed poly(vinylchloride) (PVC).

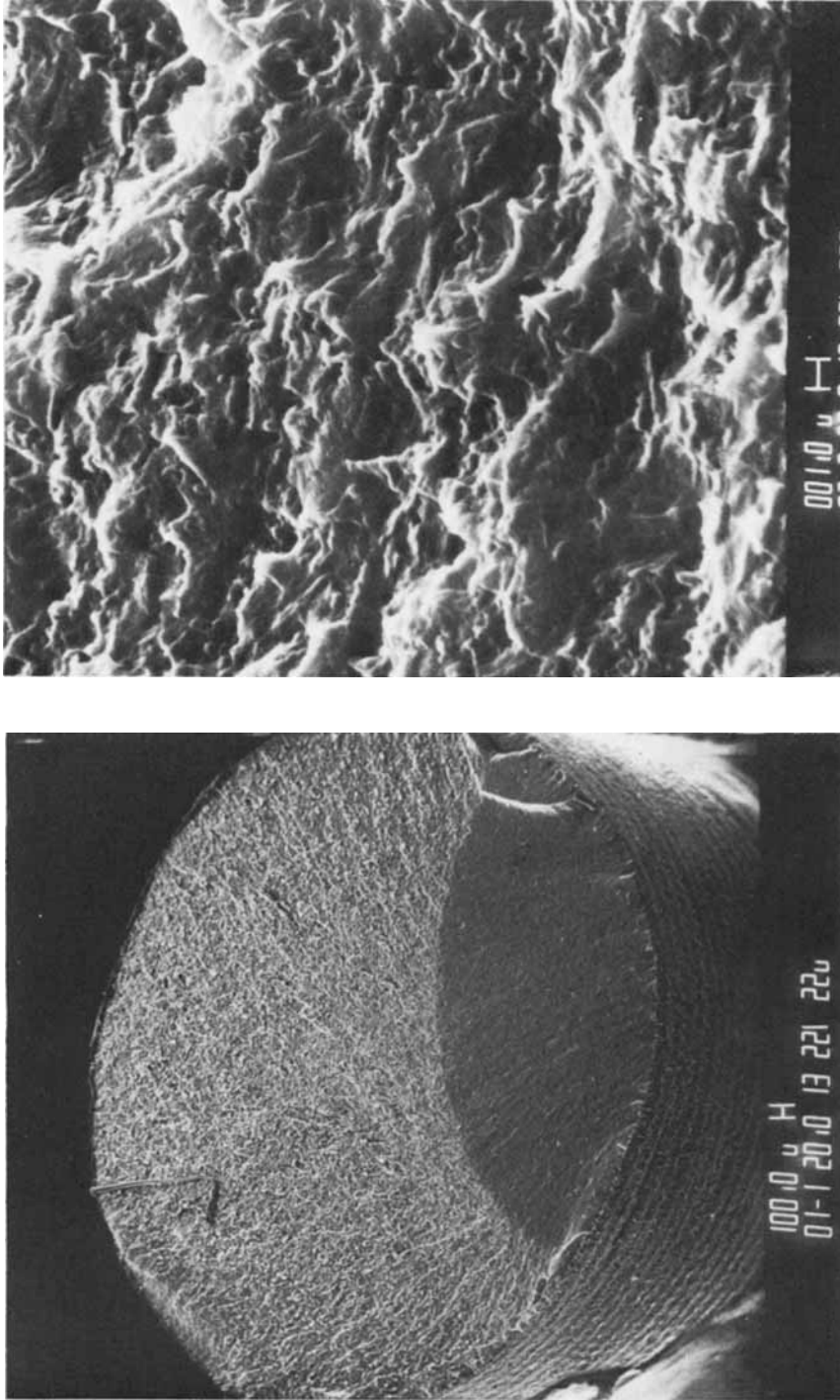


Fig. 4. SEM micrographs of tensile fracture surface of HIPS sample aged 150 h in air at 85°C: (a) low magnification view, (b) high-magnification view.

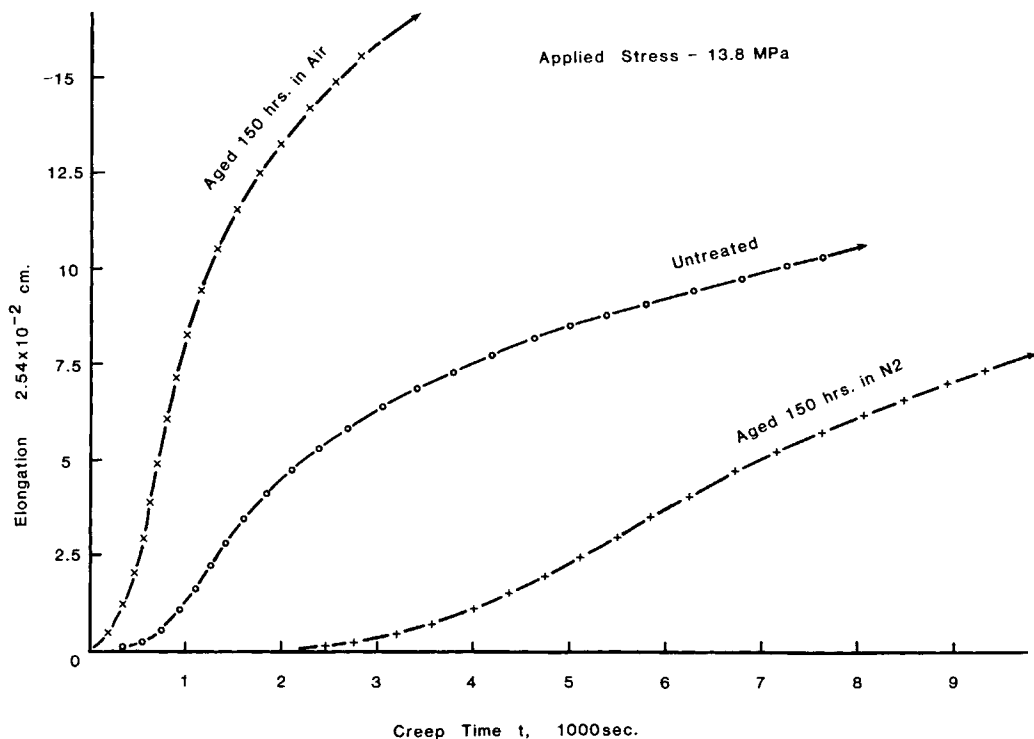


Fig. 5. Creep elongation vs. time for an untreated sample and for samples of HIPS aged in air and in N_2 and tested at a tensile stress of 13.8 MPa.

For the HIPS sample aged in air for 150 h, the tensile fracture surface, Figure 4(a), shows the two distinct regions. The dark semicircular region surrounding the surface fracture source is a slow growth region. Then, when the crack reaches a critical size, its speed greatly increases and the remainder of the fracture surface is whitened. This stress whitening is indicative of more extensive localized crazing near the fracture plane as the crack tip stress rises. A higher magnification SEM micrograph of a region on the fracture surface near the fracture source is shown in Fig. 4(b). The extensive plastic deformation that has occurred in the polymer matrix prior to fracture is very evident; and largely because of this, the second-phase particles are not sharply delineated.

The fracture surface morphology of the tensile samples that were aged in N_2 for 150 h, instead of air, are not significantly different from that of the sample fractured in air. This is not surprising as the elongation to fracture is not significantly different in the two cases, as Table II shows. The principal effect on tensile properties of aging on N_2 , instead of air, appears to be an increase in tensile strength and a reduction in plastic instability as evidenced by the lower value of the yield drop. This is attributed to a suppression of the surface oxidation effects that occur upon annealing in air.

Creep Measurements

Creep tests have been carried out on samples aged at $85^\circ C$ for various times from 1 h to 150 h in both air and nitrogen, at an applied stress of 13.8 MPa. For

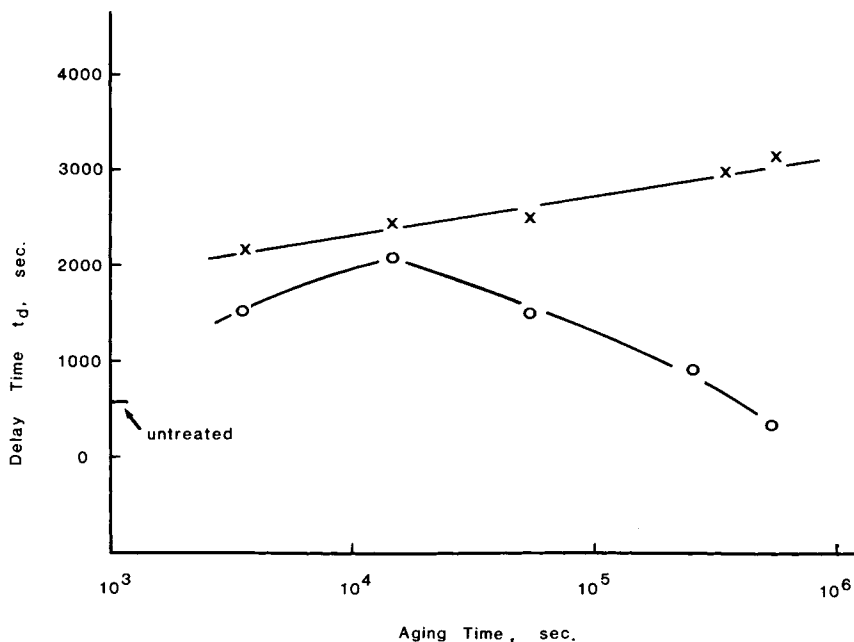


Fig. 6. Creep delay time t_d vs. aging time at 85°C for HIPS samples aged in air (O) and in N_2 (x) and tested at a tensile stress of 13.8 MPa.

the samples aged 150 h in air and in N_2 , the creep deformation that occurs after the initial elastic response is shown as a function of time in Figure 5. Data are presented also for an unannealed sample. In all three cases, the creep rate gradually increases to a maximum value and then reduces again and approaches a final steady-state value with increased time. The delay time t_d for onset of the rapid creep phase is arbitrarily determined by extrapolating the initial linear portion of each creep curve back to the horizontal axis.

Figure 5 illustrates the markedly different effects of annealing in nitrogen vs. annealing in air. The delay time t_d for onset of rapid creep deformation is greatly extended when samples are aged in N_2 , as then only physical aging effects are involved. But the delay time is decreased upon aging in air, presumably because chemical aging effects, as thermo-oxidative reactions, have now overcome the physical aging effects.

Figure 6 shows how the creep delay time varies with time of aging for samples aged in both nitrogen and air. For samples aged in N_2 , there appears to be a steady linear increase in t_d with log aging time; this is attributed to the changes in microstructure produced by the physical aging treatment. Similarly, the time to onset of rapid stress relaxation in PS upon aging to 150 h at 90°C also increased with increase of aging time.³ For the HIPS samples aged in air, Figure 6 shows that the creep delay time rises at first with time of annealing, reaches a maximum value beyond 10^4 s (~ 4 h), and then begins to decrease. This is a result of the combined effects of both physical aging (leading to improved packing, higher tensile strength and modulus, and longer time for onset of rapid creep) and of chemical aging. As noted with reference to the mechanical relaxation studies and the tensile measurements, chemical aging results in oxidative embrittlement,

TABLE III
Creep Rupture and Creep Delay Times for HIPS Aged 150 h at 85°C

Applied stress, MPa	Aging medium	Creep delay time, s	Creep rupture time, s	Strain to fracture, %
13.8	Air	395	3860	27.6
	N ₂	3200	—	
17.2	Air	54	415	25.5
	N ₂	150	7200	36.6

and this, apparently, greatly reduces the resistance of the HIPS to creep deformation.

For the samples aged in air and then tested in tensile creep at a stress of 13.8 MPa, it was possible to record a creep rupture time t_r as well as a creep delay time. However, for the samples tested in N₂, no fracture occurred during the course of the test. Additional creep tests were therefore made at a higher stress, 17.2 MPa, in order to assess the effect of the aging media on creep rupture time, as well as on creep delay time, and on elongation to fracture. The test results are summarized in Table III.

Both the creep rupture times and the creep delay times are greatly reduced at the higher stress level. This is clearly shown by the data of Table III as well

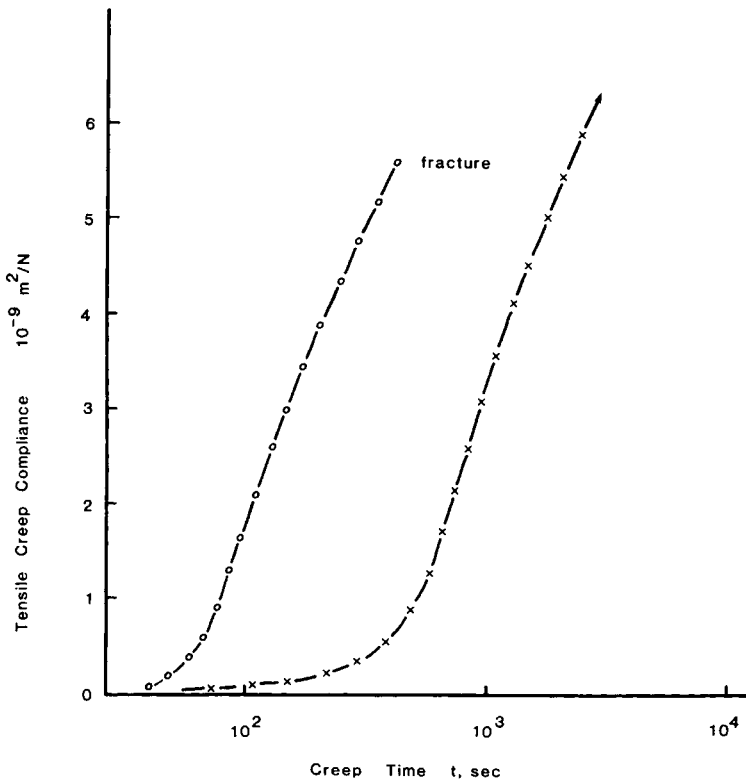


Fig. 7. Tensile creep compliance vs. creep time for HIPS samples tested at two stress values after aging for 150 h in air at 85°C: (x) 13.8 MPa; (O) 17.2 MPa.

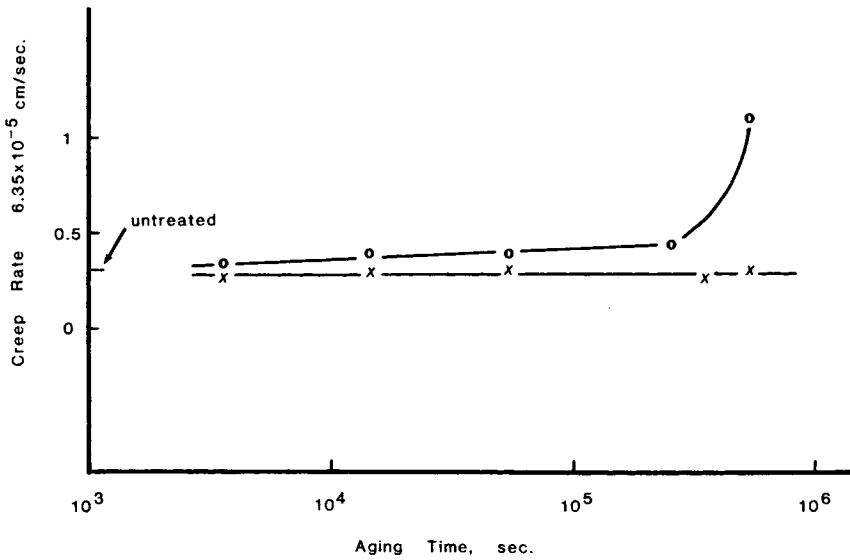


Fig. 8. Steady-state creep rate vs. aging time for HIPS samples tested at 13.8 MPa after aging at 85°C in air (O) or N₂ (x).

as by Figure 7, which depicts the creep compliance plotted against the log of the creep time for samples aged in air for 150 h. At the higher stress, there is more intensive crazing, more stress whitening, and earlier craze breakdown to form a crack. As a result, the creep compliance curve is displaced to smaller times by about one decade.

Upon aging in N₂, instead of air, both the creep delay time and the creep rupture time are considerably extended over values obtained in air, and the strain to fracture is increased by more than 40%. Once again, these effects are attributed to elimination or significant suppression of thermal-oxidative effects.

The final steady-state creep rate after long times, for an applied stress of 13.8 MPa, appears to be independent of aging time at 85°C when tests are carried out on an N₂ atmosphere. This is evident from the data shown in Figure 8. However, when the HIPS samples are aged in air, instead of N₂, the steady-state creep rate increases with increase of aging time. The nature of the variation is rather similar to that noted earlier for the shift of the low-temperature T_g transition, i.e., it increases only slowly up to about 72 h of aging and then more rapidly thereafter. Thus, oxidation effects during annealing have a strong effect on the accelerating stage of creep, and also on the final steady-state creep rate, and on the creep rupture time.

The nature of creep fracture is not significantly different than that observed in tension. SEM micrographs have been taken of creep samples fractured at a stress of 17.2 MPa after aging for 150 h in either air or N₂. At low magnification, the fracture surfaces show two distinct regions akin to those shown in Fig. 4(a). There is a darker slow growth region followed by a whiter and more textured fast growth region. In creep, as distinct from tensile loading, the slow growth region is slightly larger, and the demarcation line separating the two regions is closer to a straight line than to a circular front.

High magnification micrographs of a portion of the fracture surface near to

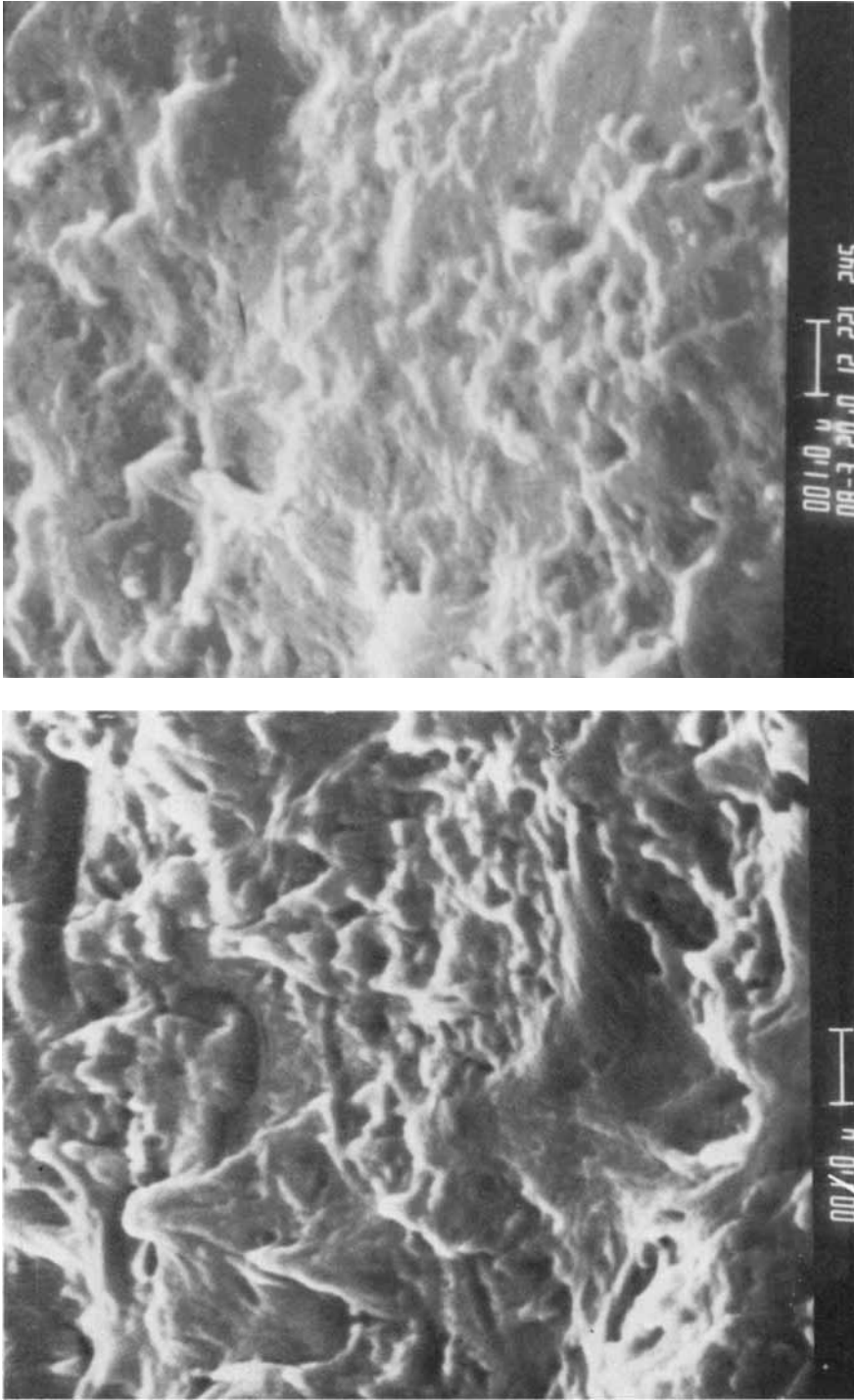


Fig. 9. SEM micrographs of creep fracture surfaces of HIPS samples tested at 17.2 MPa after aging for 150 hrs at 85°C: (a) aged in N_2 , (b) aged in air.

the source are shown in Figure 9(a), for the sample aged in N_2 and in Figure 9(b), for the sample aged in air. For the sample aged in N_2 , matrix deformation is greater, and the fibrillar elements appear to be more highly drawn before fracture. Both micrographs show a rather ill-defined, fractured, second-phase particle in the central region. The particle is somewhat better defined and shows more evidence of ductile rubber tearing in the case of the sample aged in the nonoxidizing atmosphere. It is speculated that oxidation of the polybutadiene rubber phase inhibits the relaxation of the rubber particles, less energy is required for initiating a crack,⁵ and hence time to fracture is reduced.

Fatigue Measurements

Table IV presents the results of the fatigue tests made in tension-compression at a stress amplitude of 13.8 MPa. For samples aged in N_2 , tests were made on samples that had been aged 1, 4, 96, and 150 h; while for samples aged in air, tests were only made on samples aged for 150 h. It appears that the mean fatigue lifetime increases at first with increasing time of aging but then gradually diminishes as aging times become long. A similar trend has been reported for fatigue tests of annealed HIPS samples, made on a different fatigue test apparatus.⁸ For the samples aged 150 h in air, the mean lifetime is only a little lower than for the samples annealed in N_2 .

The situation for fatigue performance is thus somewhat different than for creep performance, as changing the annealing medium from air to nitrogen, and presumably suppressing the chemical oxidative reactions and resulting embrittlement, leads to only a 10% or so improvement in lifetime. It is known that fatigue resistance is much more dependent upon surface condition and perfection than is creep.^{20,21} Hence, even a small amount of oxygen present in the nitrogen gas may be sufficient to cause some surface oxidation and resulting embrittlement. It has been noted that even technical-grade nitrogen contains enough oxygen to cause some hydroperoxidation of HIPS films when these are subject to elevated temperature exposure at 100°C.¹⁴ Hence upon annealing HIPS in commercial-grade N_2 , the surface of the test sample and, in particular, the second-phase particles on or near the surface may become sufficiently oxidized to cause earlier crack development and hence lower fatigue lifetime.

HIPS behaves quite differently in tension-compression fatigue loading than in simple tension loading. For example, in a tension test stress whitening of the gauge section begins to develop as the stress rises toward the yield value, and then

TABLE IV
Fatigue Data on HIPS Samples Aged at 85°C

Aging medium	Aging time, h	Number of samples	Mean fatigue life, cycles
None	—	5	21,800
N_2	1	4	22,200
	4	4	16,300
	96	4	9,220
	150	4	8,850
	150	3	8,140
Air	150	3	8,140

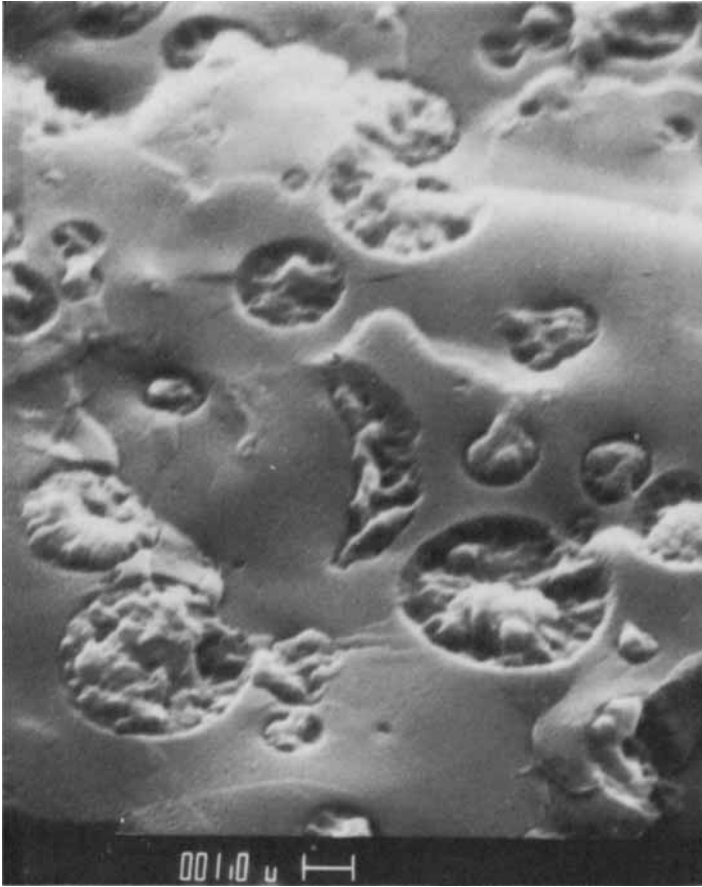


Fig. 10. High-magnification SEM micrograph of a portion of the fatigue fracture surface of a HIPS sample tested at an alternating stress amplitude of 13.8 MPa after aging in N_2 for 150 h at 85°C.

the stress whitening greatly intensifies as the plastic strain increases. The crazes that form throughout the volume of the sample, as a result of the stress concentration effect of the rubber particles, are sufficiently stable so that large plastic deformation can occur prior to fracture. Hence, the performance of tensile specimens, as well as creep specimens where similar intense crazing and stress whitening develop, reflects largely the bulk behavior of the material. In fatigue, on the other hand, stress whitening is absent. Once a craze forms at the most severe surface flaw, it soon breaks down under cyclic stressing to form a crack. Hence, in rubber-modified polymers, as well as in unmodified glassy polymers, fatigue performance is governed to a great extent by surface condition.

The fatigue fracture surface of HIPS differs appreciably from that observed in creep or tensile fracture and also from that observed in the fatigue fracture of the PS homopolymer. In the latter case, as shown elsewhere,^{11,20} there is a smooth semicircular region, indicative of single craze development and growth, surrounding the surface flaw where the crack initiated. In HIPS, however, while the fracture develops from a surface source, the area surrounding it is highly textured.⁸ This morphology presumably arises because many matrix crazes

develop on slightly different planes around the equator of the dispersed rubber particles and, once a microcrack is generated in one of these crazes—possibly by development of a large cavity in the less occluded rubber particles, as discussed by Donald and Kramer²²—it progresses by jumping from one craze plane to another.

A high-magnification view of the fracture surface of a HIPS sample aged 150 h in N₂ at 85°C prior to testing is shown in Figure 10. The comparatively smooth surface of the matrix surrounding the second phase particles is indicative of fracture through preexisting crazes. The particles, unlike those on the fracture surface of samples broken in tension or tensile creep, are well defined, and the composite nature of them is evident. Adhesion of the particles to the matrix is high; and, at some edges, ligaments can be seen connecting the second-phase particle to the matrix. One interesting feature of this micrograph is that it shows that some of the particles, such as the crescent-shaped one in the center of the micrograph, are nonspherical. For the samples aged 150 h in air instead of N₂, rather similar morphology is obtained; and, as noted in Table IV, the average fatigue lifetime is little affected by the change in medium.

CONCLUSIONS

(1) Elevated-temperature aging of HIPS in air involves both a physical aging process and a chemical aging process.

(2) For short times of aging, the physical aging process appears to dominate. This results in a higher tensile stress, in a longer delay time to accelerated creep, and a slightly higher fatigue life.

(3) For longer times of aging, the chemical aging process begins to dominate. Due largely to oxidative attack on the rubber phase, the tensile strength falls, the creep delay time is reached earlier, and the fatigue life reduces.

(4) Aging in air causes the rubber phase T_g to move to higher temperatures while the loss peak broadens. These effects are attributed to increased cross-linking caused by interaction of oxygen with double bonds present in the polybutadiene phase.

(5) Aging in nitrogen has essentially no effect on the location of the rubber-phase T_g , but it does lead to a higher modulus, a longer time to accelerating creep and to creep rupture, and a higher tensile strength. However, ductility and fatigue life are reduced.

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